Multifunctional 2D- Materials: Selenides and Halides

N. B. Singh, Bradley Arnold, and Fow-Sen Choa
University of Maryland, Baltimore County
Baltimore, MD 21250, USA

and

Ching Hua Su
EM31, NASA Marshall Space Flight Center, Huntsville, AL 35812

Email: singna@umbc.edu

Novel materials Bring Revolution for Devices and hence systems

Multifunctional 2D- Materials: Selenides and Halides

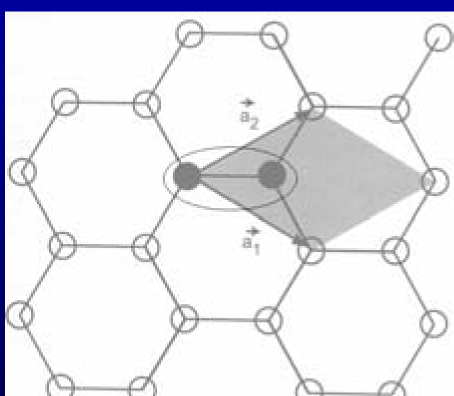
Objectives:

The main objective is to introduce some new multifunctional 2D materials and compare their performance with bulk, thin film, micro and nano crystals

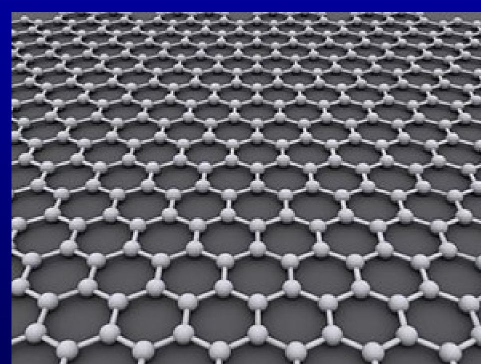
Novel materials Bring Revolution for Devices and hence systems

Huge number of papers have been published Where are big bang applications……?

- Since the isolation of graphene, a single-layer of graphite, in 2004, a large amount of research has been directed at isolating other 2D materials due to their unusual characteristics
- Applications such as photovoltaics, semiconductors, electrodes and water purification.
- It is a source of remarkable properties, such as very high electronic conductivity and mobility.
- Its breaking strength is 200 times greater than steel.



Lattice structure of graphene in real space

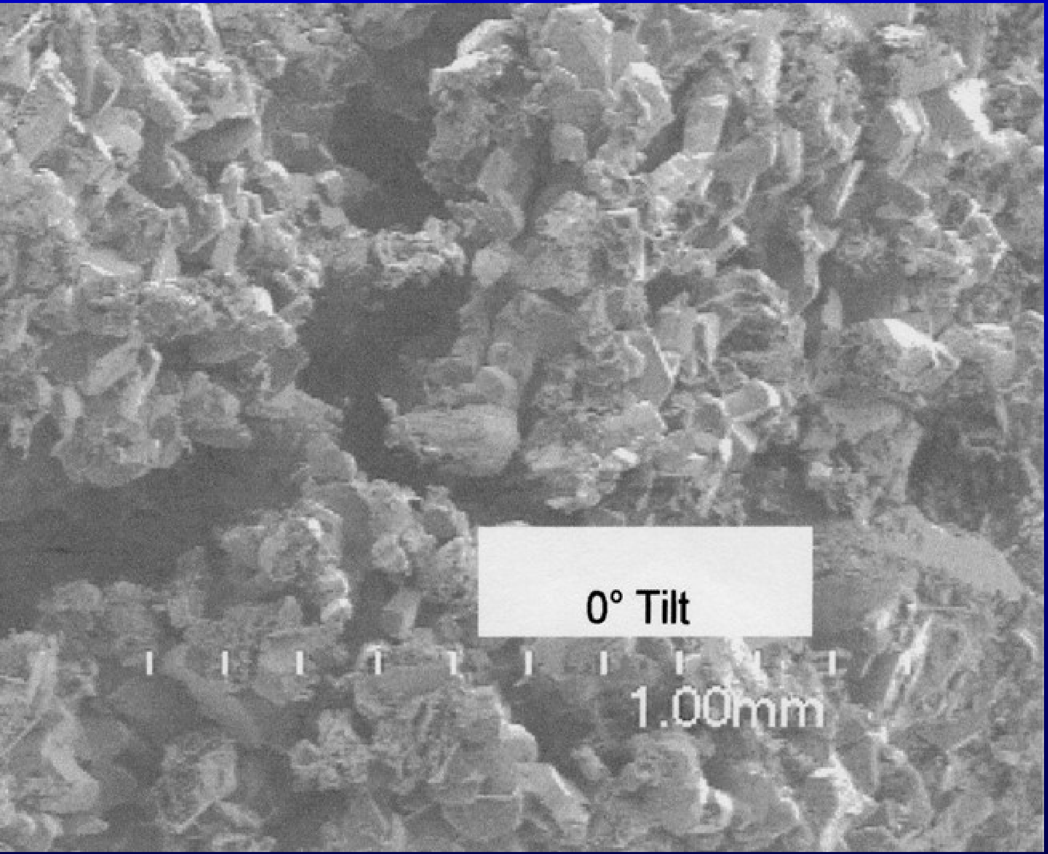


The atomic arrangements are in honeycomb mode in graphene

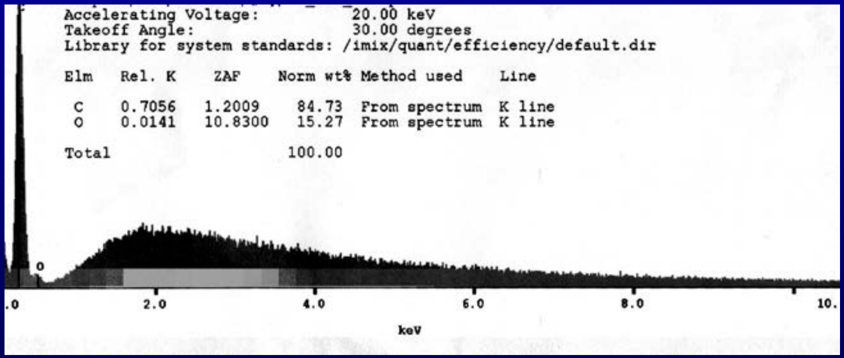
Applications ?

2D structures were known in materials and were referred as layered materials

We have grown and characterized morphology and composition of wrinkled multi layer sample of Graphene



Traces of oxygen was determined because annealing of SiC was performed in unevaluated furnace

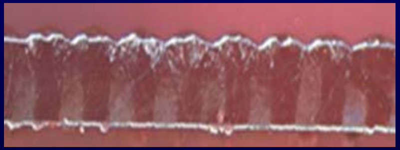


Singh et al (unpublished) other 2D crystals can be fabricated into devices

Motivation for Selenide Crystals

- Enables scaling of power and spectral range
  - Transparency from 0.6 to 20 μm
  - Extremely low intrinsic absorption (≤ 0.001 cm^{-1} from 1 to 16 μm
  - Large "d_{eff}" coefficient
- Bulk Materials
  - Binary Selenide Crystals; GaSe (GSe)
  - Ternary Selenide Crystals; Tl3AsSe3 (TAS)
  - Quaternary Selenide Crystals; Ag $GaGe_3Se_7$ (AGGSe)

- Quassi Phase Matched Materials
  - Zinc Selenide Crystals



- Laser Host Materials
  - Halide based laser host (Lead Bromide)

Selenides have huge potential for device applications and have lowest absorption coefficient in wide transparency range

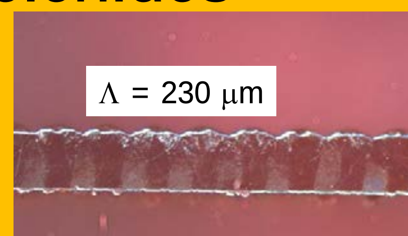
Optoelectronic devices, LEDs, Solar cells, sensors, Laser diodes, THz sensors

Substrates and transparent electrodes

High power RF and electronic devices and components

Applications of Selenides

Self compensating gas sensors



Lasers and Optical pumping

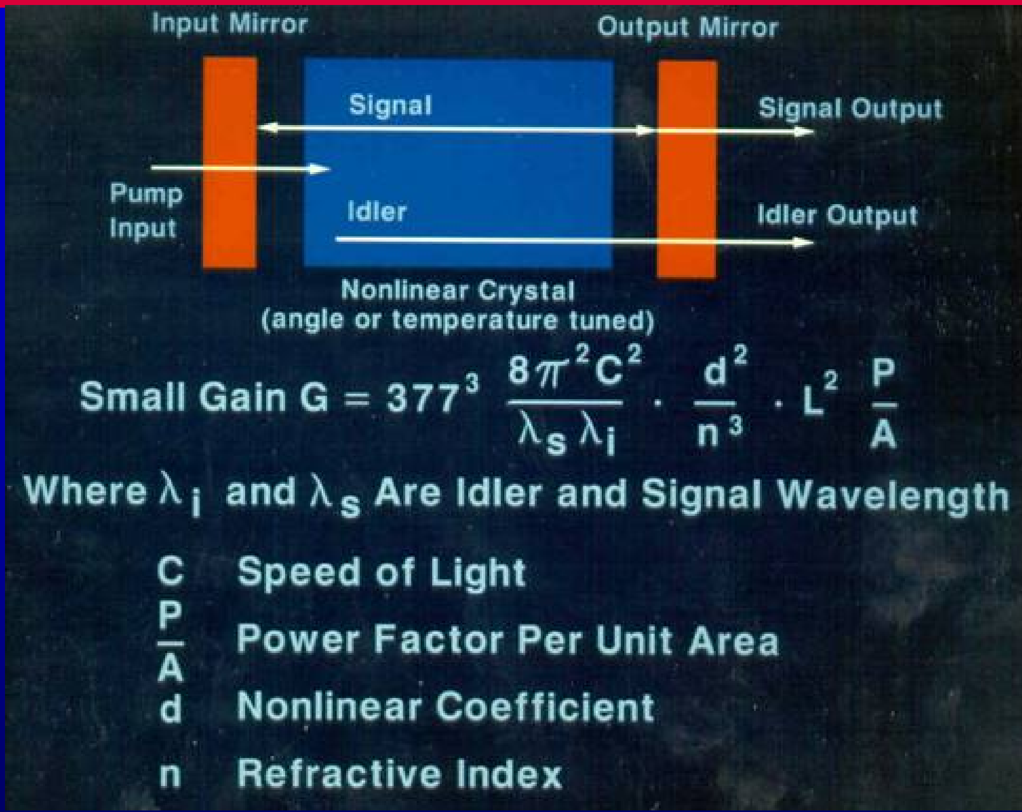
Bulk, thin film, nano and QPM off II-VI compounds have potential

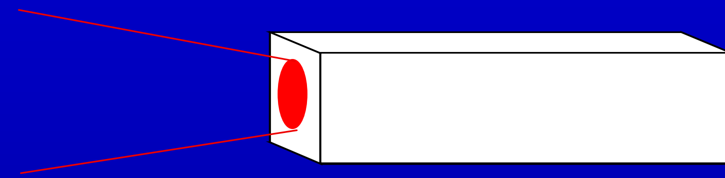
Piezoelectric and pyroelectric devices

SAW devices such as filters, oscillators

Electronic FETs

NLO Requirements for direct pumping by 1.06 μm laser





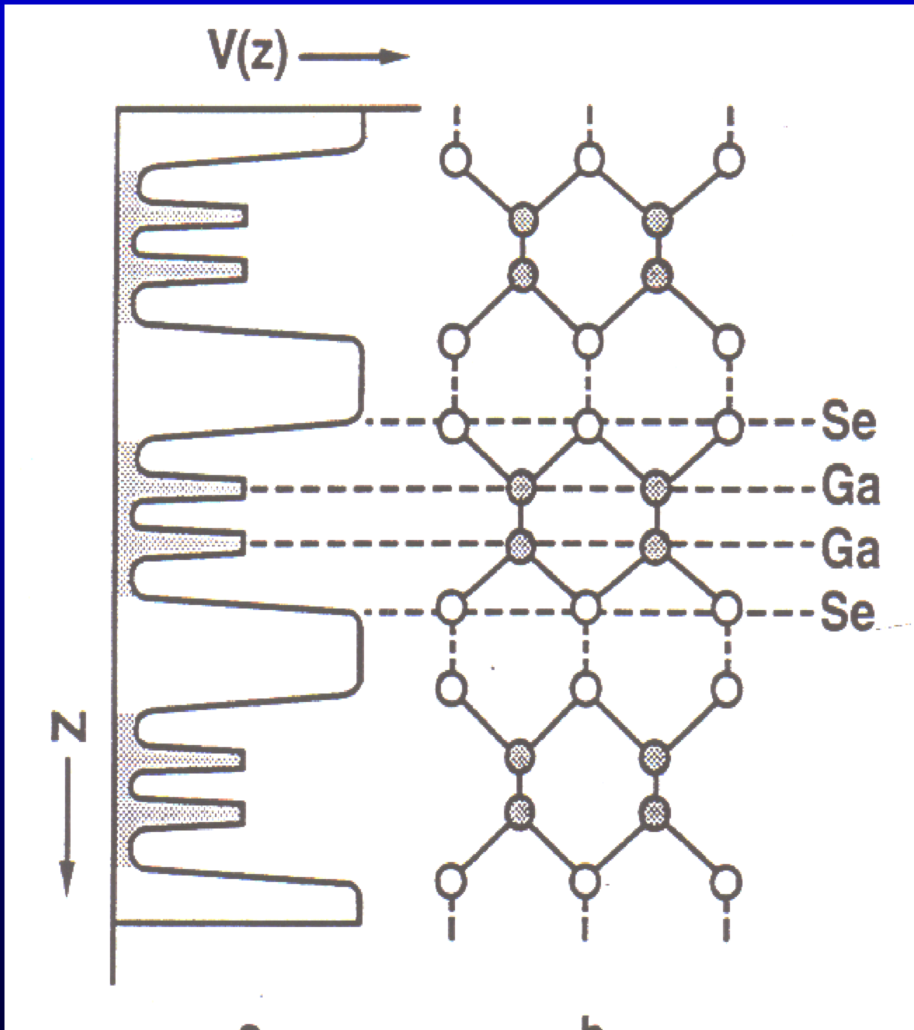
Birefringent Materials and Required characteristics

Benefits of Ag-Ga-Ge-Se System

- Damage T-hold > 3 J/cm^2
- Small Walk-off
- High d^2/n^3 (180)
- Low cost
- Adhering coatings
- Transparency 0.65 to 18 μm

Transparency range can be designed by Selenium

Why New Derivatives? Very weak bonding along C direction causes cleaving

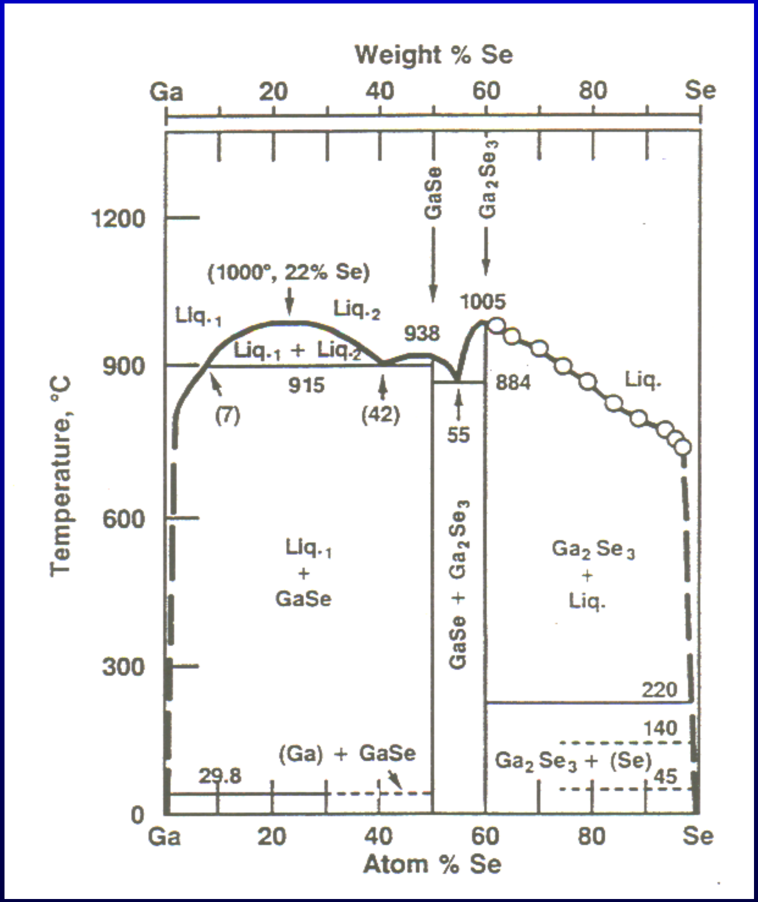


Layered structures along - c and covalent along –a directio

GaSe is a very good fabricable 2D material.

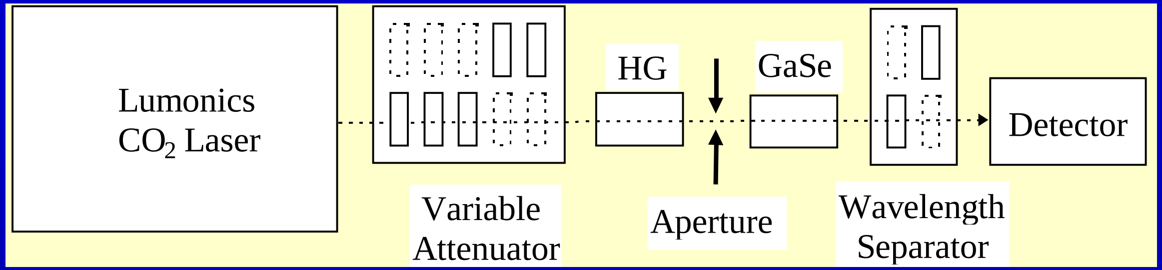
Phase diagram shows two congruent compounds

- GaSe is a congruent compound which melts at 938C.
- Charge for crystal growth was prepared by combining Ga and Se
- Both Ga and Se were further purified before reacting
- Crystals were grown in Bridgman geometry
- In and other dopants were used in GaSe

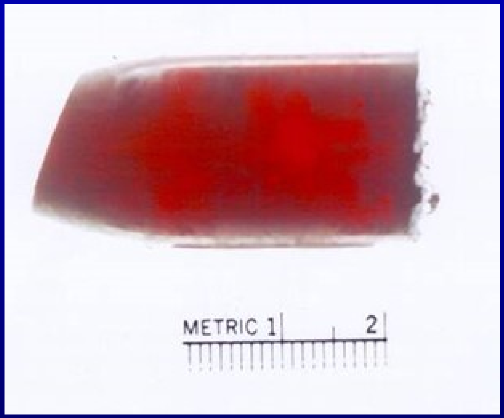


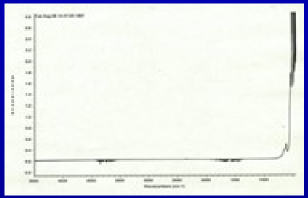
There are congruent compositions in Ga-Se system

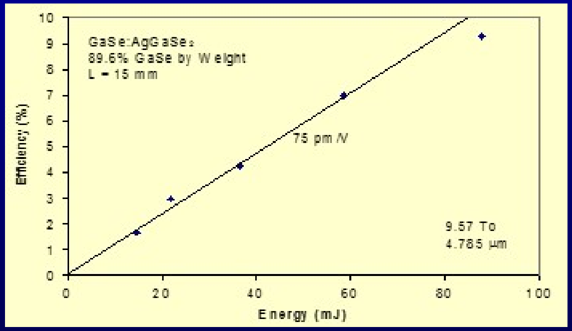
Pure GaSe has very large NLO Merit (d^2/n^3) but peels like mica when fabricated



Lumonics 203 CO_2 laser on 9P(22) at 9.569 mm
Fundamental intensity varied with attenuators
Output measured with pyroelectric detector
Second harmonic produced with TAS crystal
Third, fourth, and OPO mixing in GaSe crystal
SHG also measured directly in GaSe







Oscillator: 100 mJ/Pulse

9.25 mm, 20 nsec FWHM

~ 100 mJ/Pulse, < 50 kHz

Amplifier: ~10 dB Gain

~ 1 mJ/Pulse, < 50 Watts

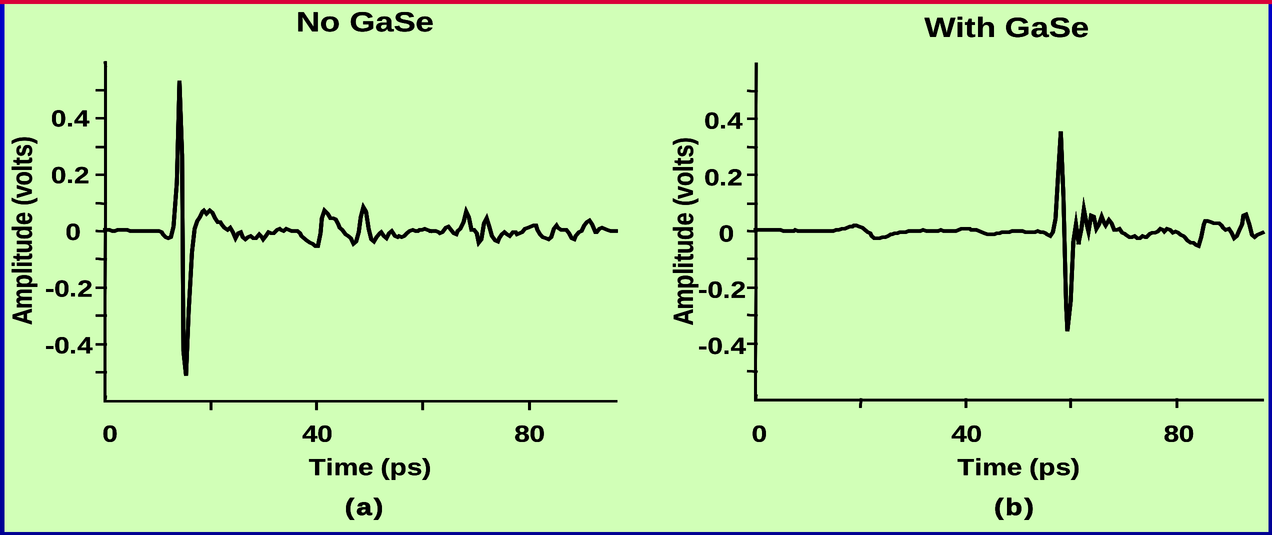
Procedure: Focus to 150 μm spot in crystal, and measure 9.25 and 4.625 μm power using sapphire plate to block fundamental

Pure GaSe showed "d" coefficient up to 75pm/V

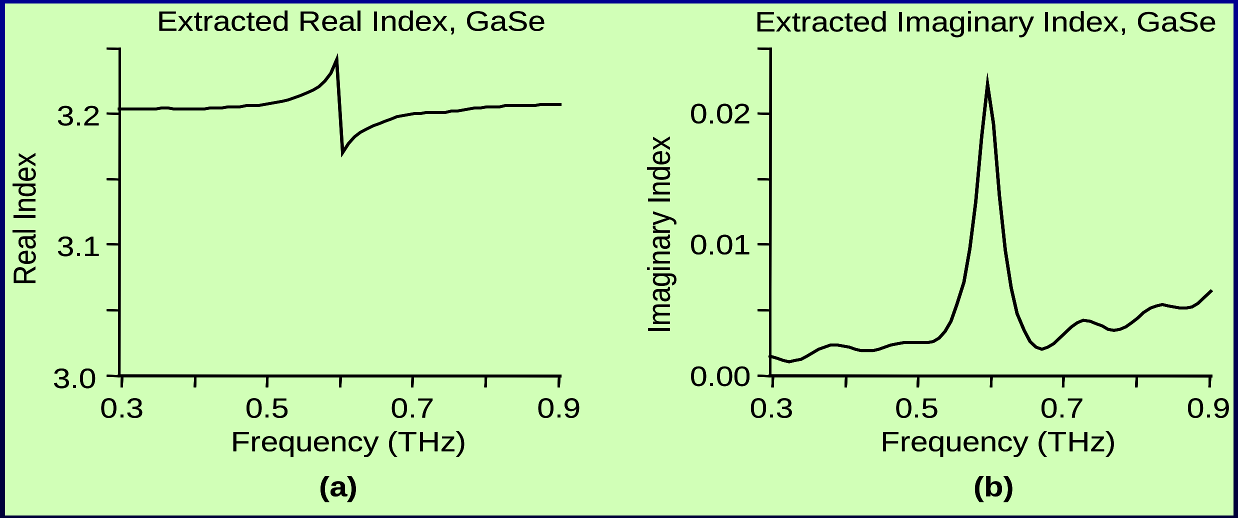
*>3.7 J/cm^2 at 9.25 mm and 20 nsec pulses (>180 MW/cm^2)
* >86 kW/cm^2 average power at 9.25mm

GaSe has strong cleavage, "d" is significantly reduced in doped GaSe

GaSe is an excellent THz sesnsor material



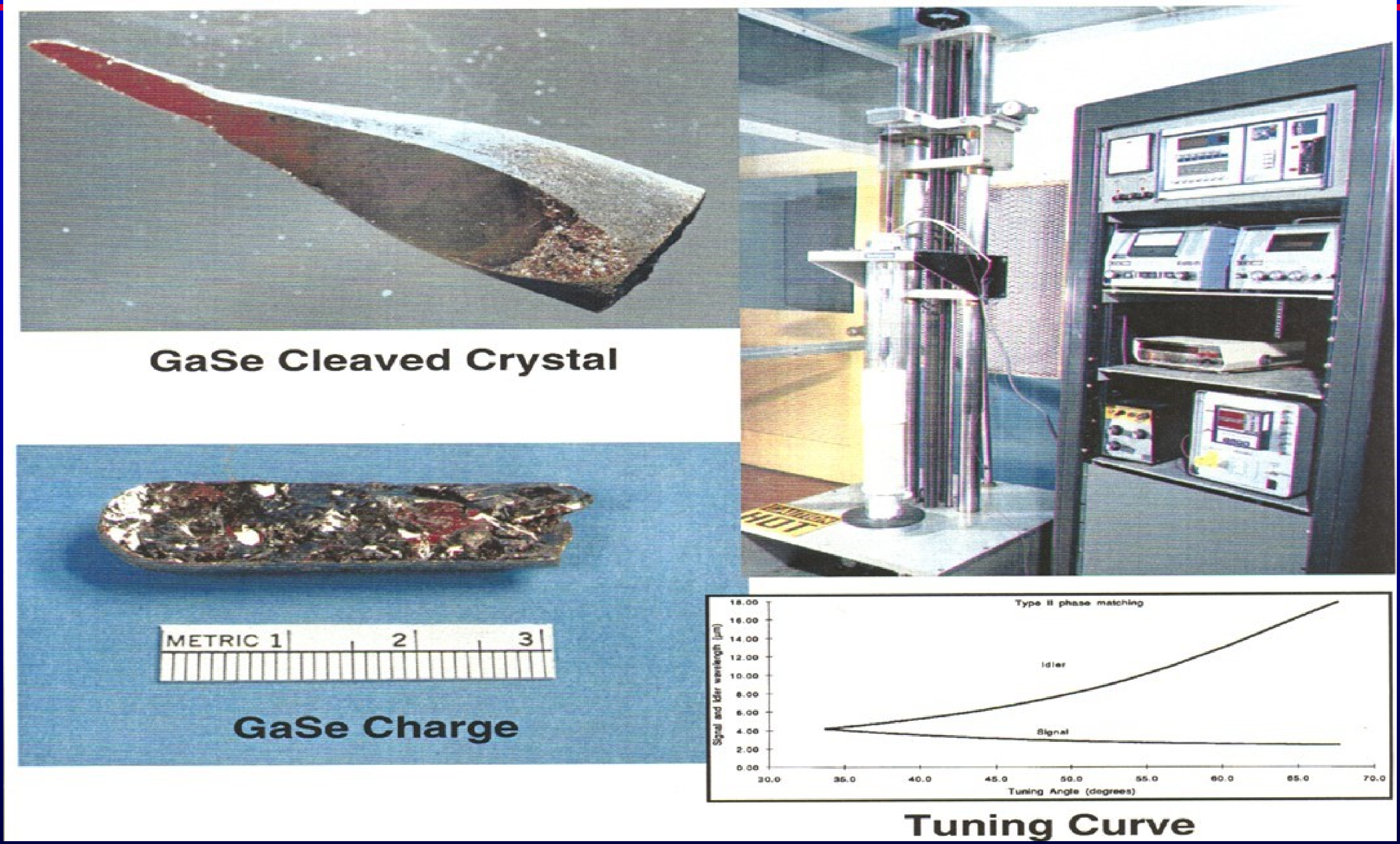
Terahertz waveforms: (a) without and (b) with the GaSe sample



Index of refraction extracted from transmission measurements of GaSe (a) real part (b) imaginary part. The y-scale of the real index spans a range of 0.25, while the imaginary index spans a range of only 0.025.

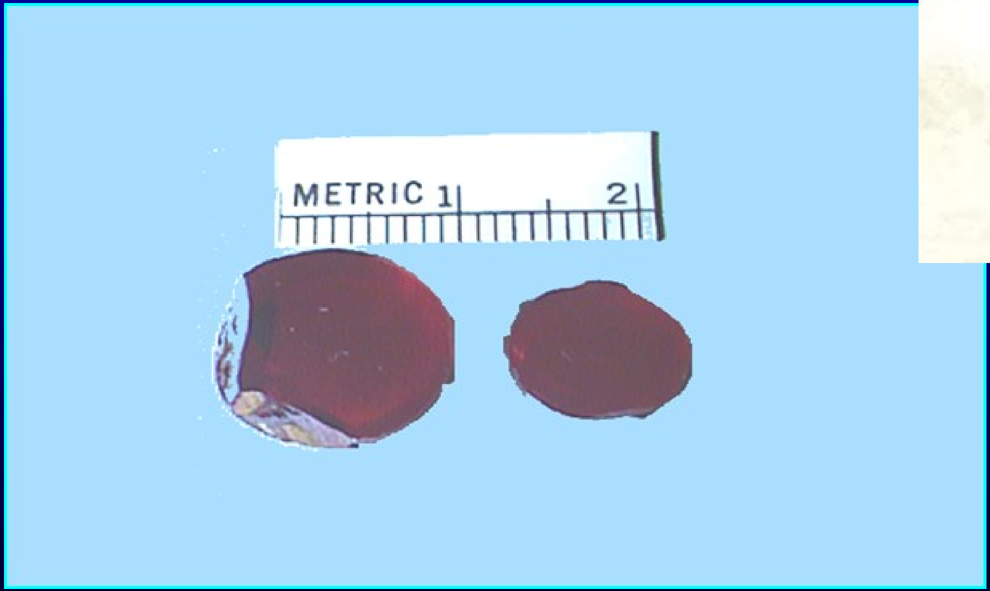
THz sensor, Singh et al, J. Optical Engineering, 45(9), 094002-1 (2006).

GaSe Crystal is can be considered as a bundle of layers

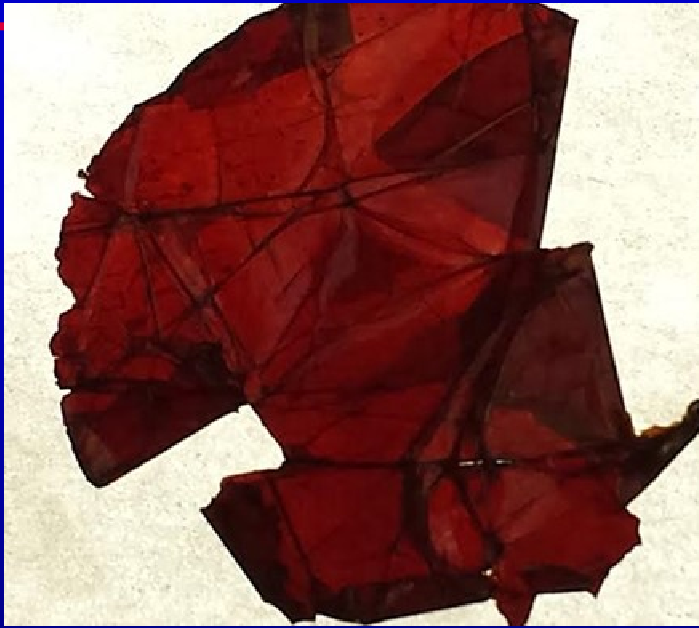


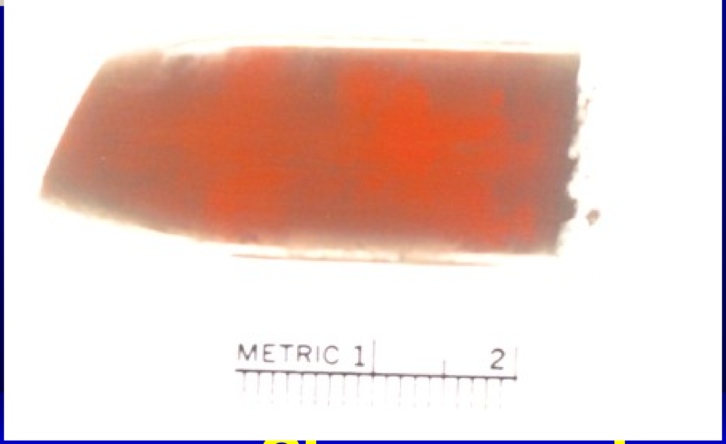
GaSe composition showed phase matching

Thallium gallium selenide is another material with layered structures



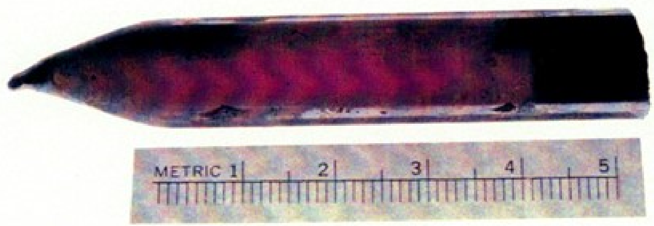
Extremely thin layer of Gallium Selenide





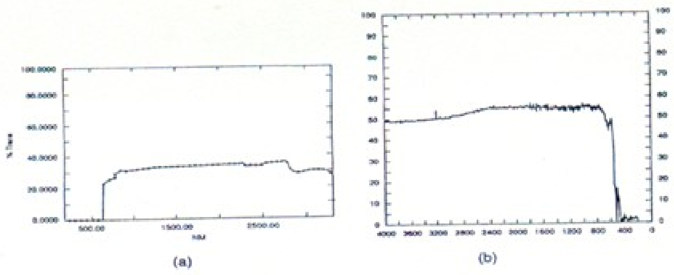
Cleavage plane is visible in pure crystal.
Doped crystals increase forces between Vander Waal bonds

Gallium Selenide for NLO Applications

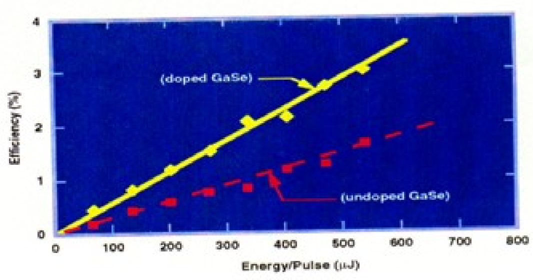


As-grown GaSe

GaSe prism



Transmission curve for uncoated GaSe in (a) Near-IR, and (b) Far-IR wavelength region

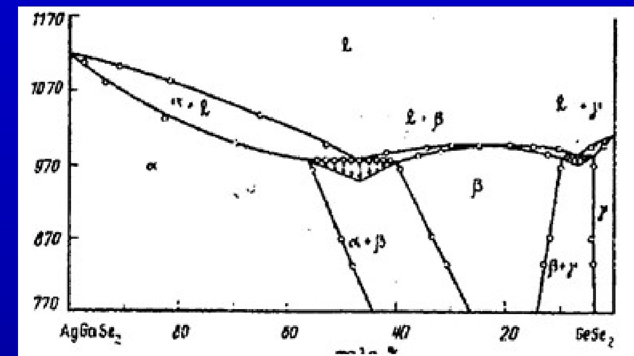


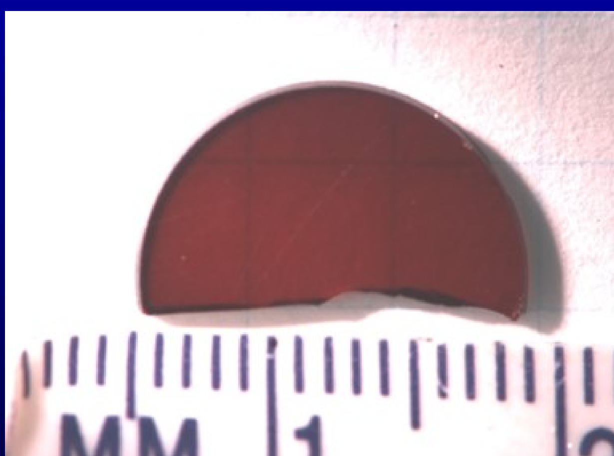
SHG output of 4 mm GaSe samples

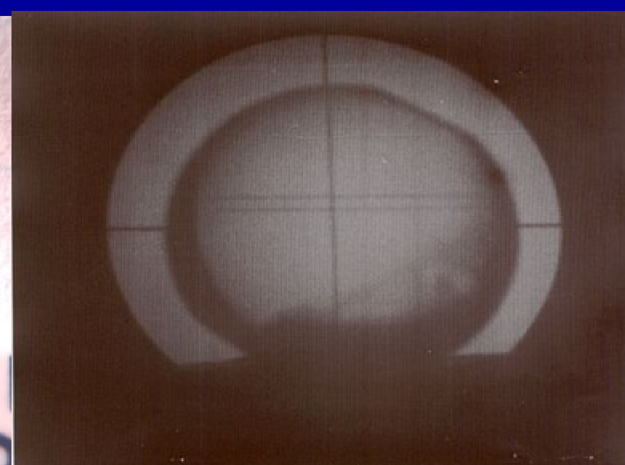
Performance of modified material: We doped with Indium

AgGaGe$_3$ Se$_8$ Crystals were synthesized and grown for SHG demonstration

- Three members of AgGaGe$_n$ Se$_{(2n+2)}$ family are studied and some data available in literature:
  - AgGaGeSe$_4$
  - AgGaGe$_3$ Se$_8$
  - AgGaGe$_5$ Se$_{12}$



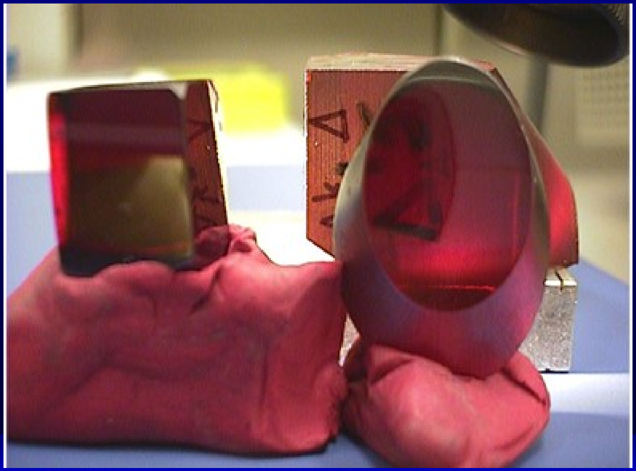




Quatenary 2D materials were slightly stronger in –C direction

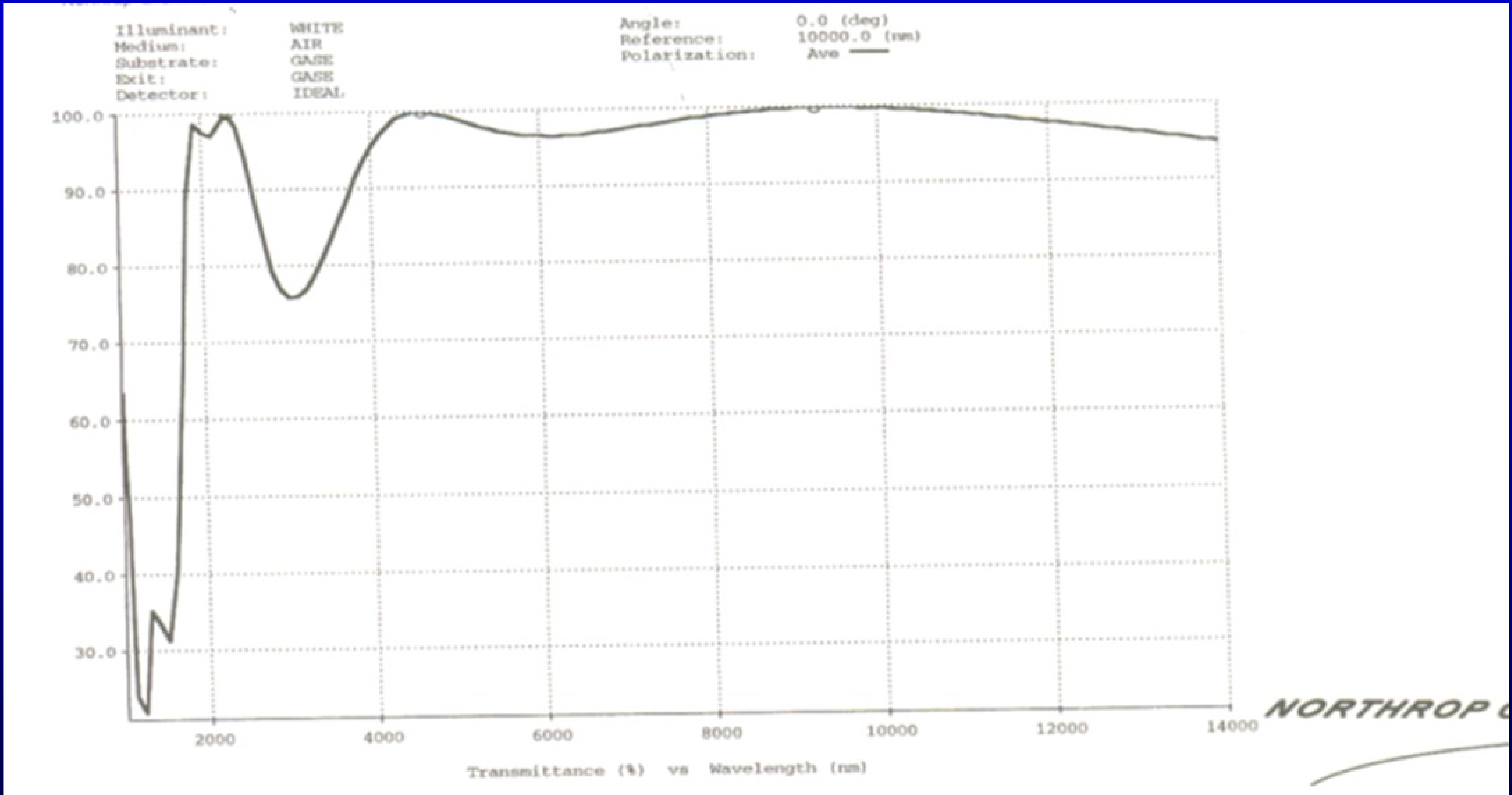
$AgGaGe_3Se_8$ Crystal Could be grown and fabricated due to stronger Vander Waal bonds

As-grown crystals were up to 6 cm long



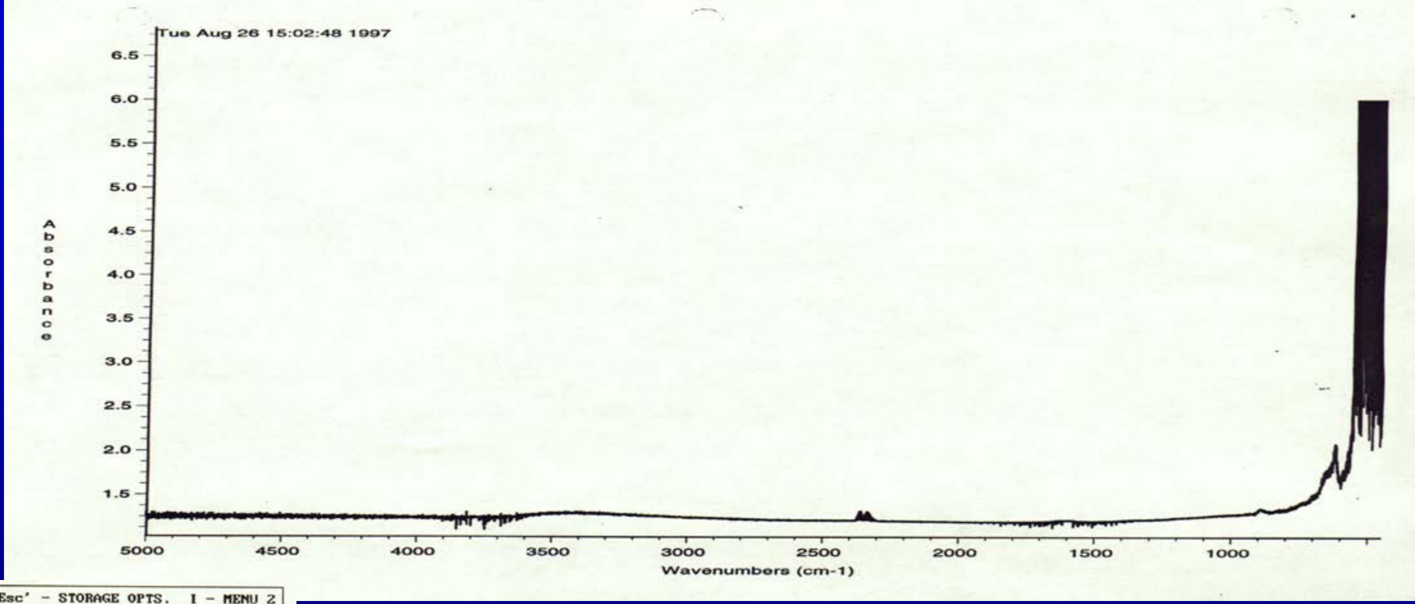
Single crystals were grown by Bridgman method

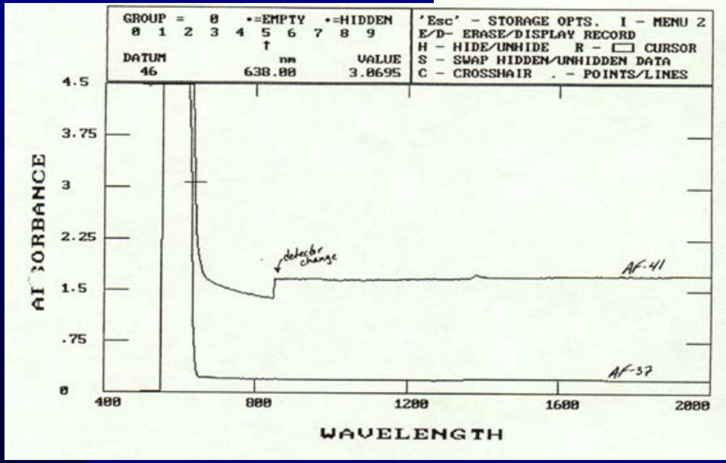
Gallium Selenide



Wide transparency range AR coatings

Gallium Selenide and its derivatives have lowest absorption



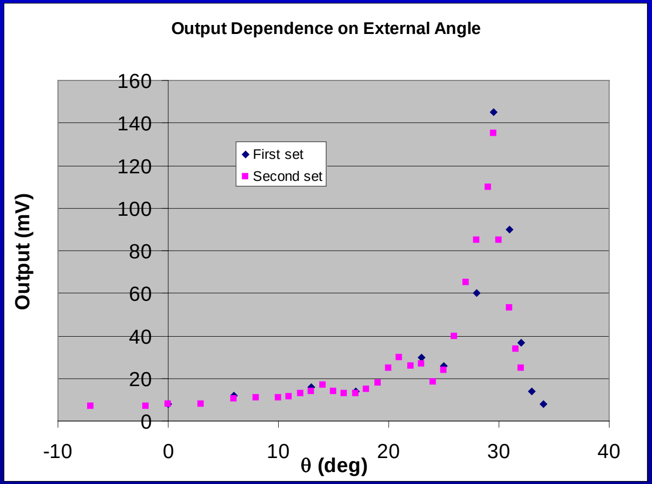


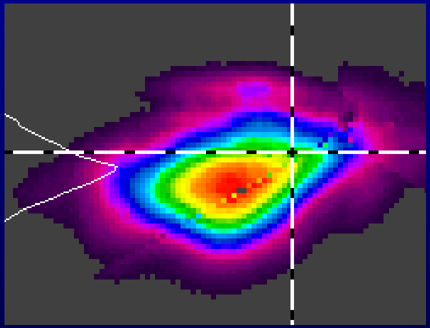
Lowest absorption in any optical NLO, THZ crystal

Experimental Observations and Measured Signals

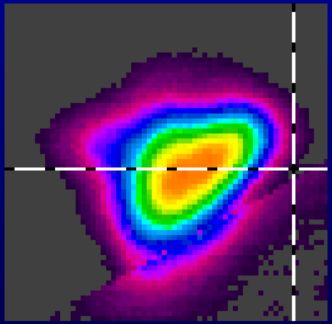
- Sample transmits beam with very low scattering
- Possibly higher damage threshold than previous selenide samples
- Optical transmission seems good, especially if we compare to expected Fresnel losses for AgGaSe2 (about 19% per face)
- Transmission measured for different yaw, pitch angles; last row shows where obtained greatest NLO signal; lower transmission and degraded beam image shows probable beam clipping.

ϕ (deg)	θ (deg)	Transmission
0	0	0.64
10	0	0.67
10	30	0.51

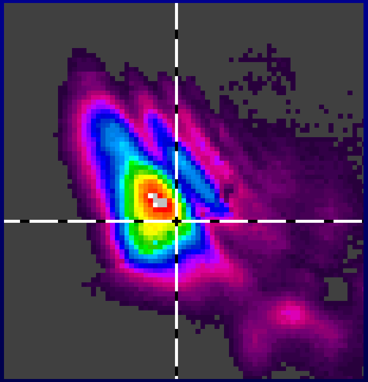




Incident beam, 9.27 μm



Transmitted 9.27 μm, $\phi \approx 10°$, $\theta \approx 0°$ external angles

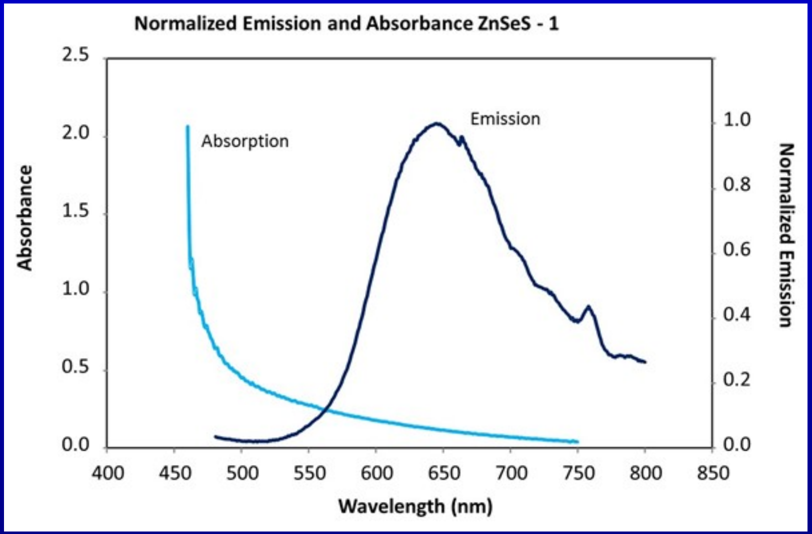


Transmitted 9.27 μm, $\phi \approx 10°$, $\theta \approx 30°$ external angles

Sample showed low scattering. "d" = 30pm/V

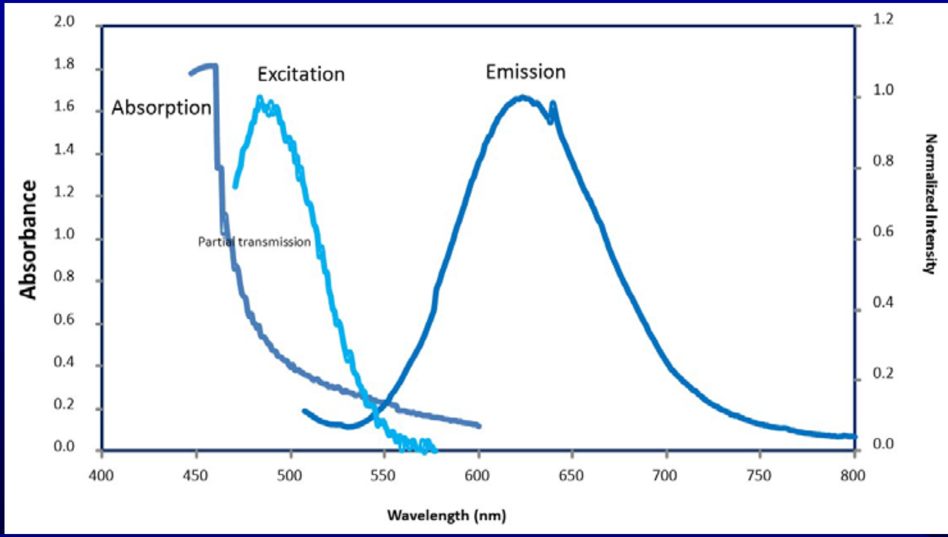
- Appears partially limited by aperture since peak of signal observed at ~30 deg off normal incidence (see image previous slide)
- Walkoff: for AgGaSe2 and 9.27 μm -> 4.63 μm + 4.63 μm SHG interaction walkoff angle is 12.45 mrad
  - This gives l_a = 1.4 cm aperture length, slightly below actual 1.5 cm length of crystal
- From SNLO, $AgGaSe_2$ angular tolerance is 14.33 mrad·cm (half-width to zero),so expected (external) acceptance angle for this crystal length is 1.1°, which is close to the measured value of 1.5 °.

Spectral characteristics of ZnSeS



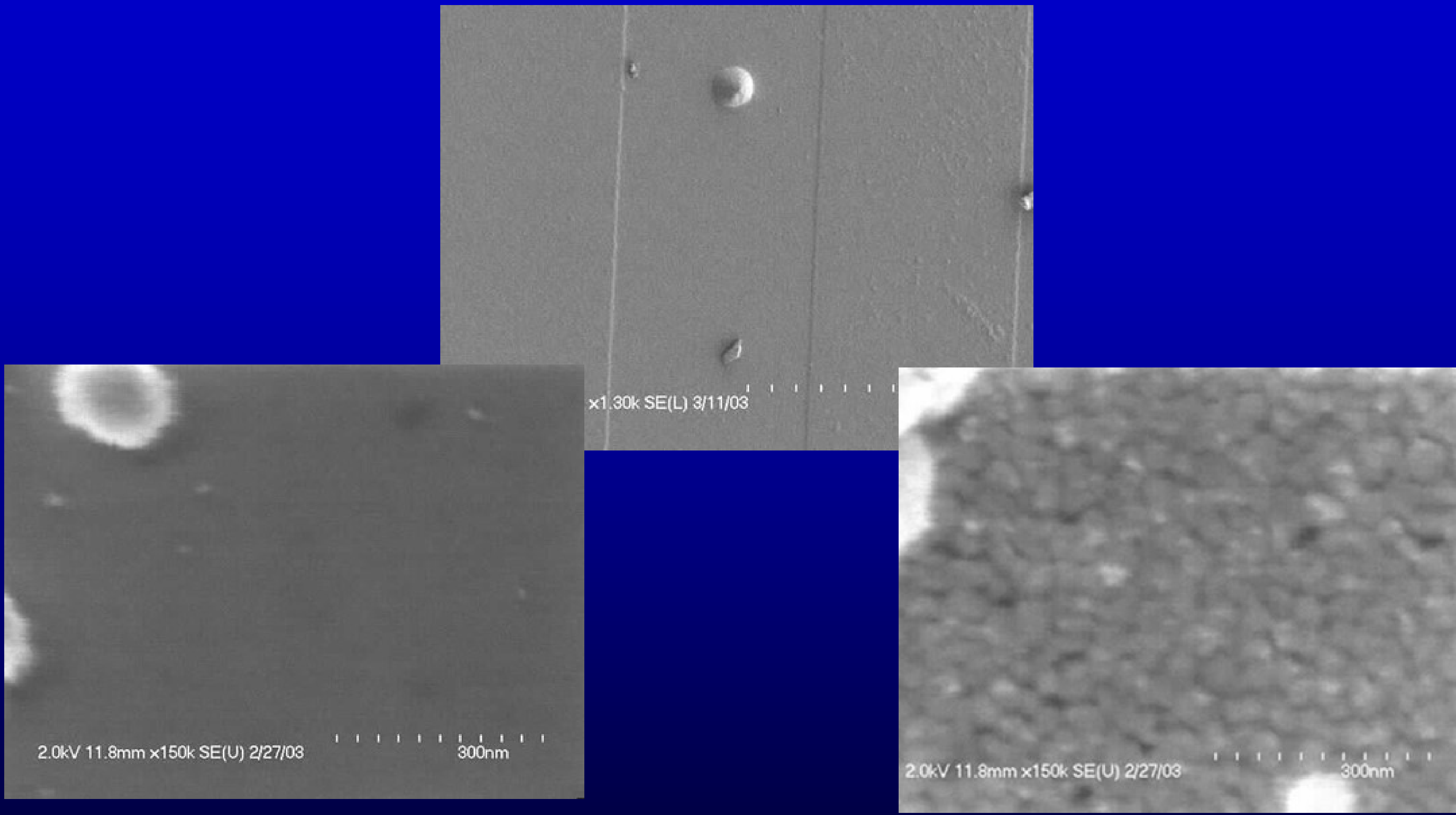
Normalized absorbance and emission spectra with ZnSeS-1. The overlapped region occurs between 450 and 550 nm (2.70eV) with emission maximum near 610-630 nm.

The data of crystal ZnSeS-2 shows detailed absorption, excitation and emission spectra without filter similar to that of crystal ZnSeS-1.



There are congruent compositions in ZnSe system

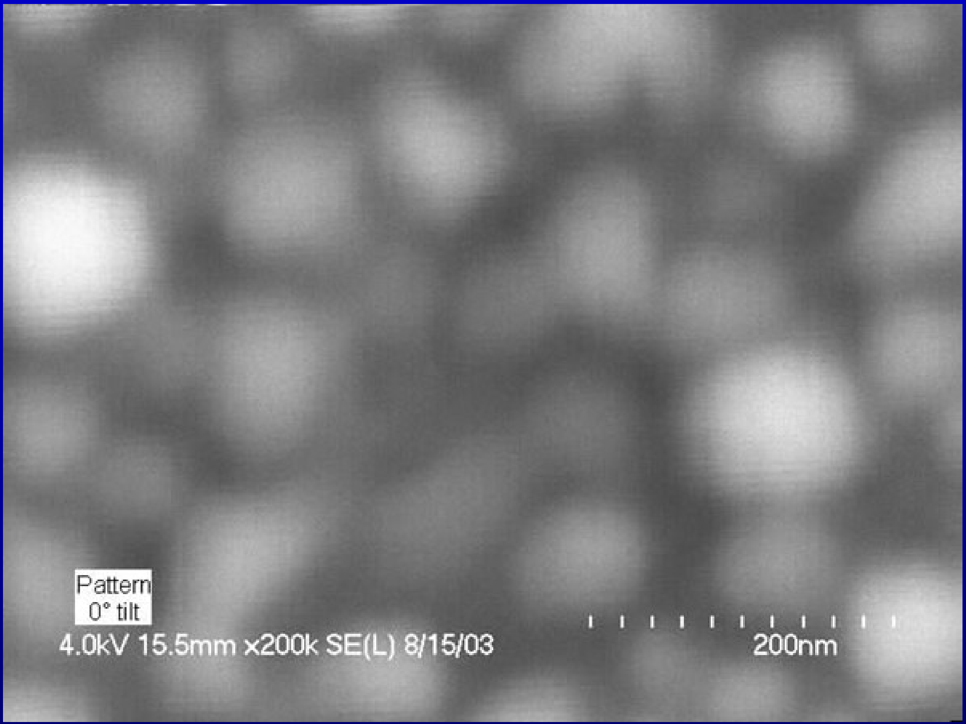
Nanomorphology of ZnSe on patterned and unpatterned substrates

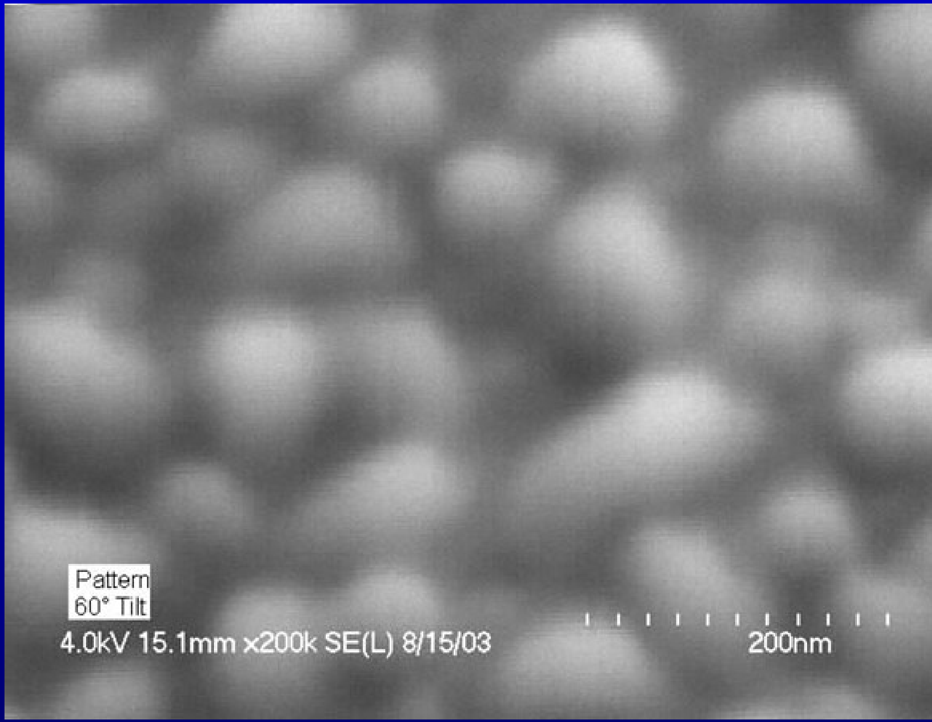


Morphology of (a) ZnSe on patterned and non-patterned portions of substrate (b) epitaxial and smooth film on non-patterned GaAs and (c) nano particles of ZnSe on patterned substrate

Materials are based on strategic requirements of DoD, DHS and DoE

Morphology of nanolayers

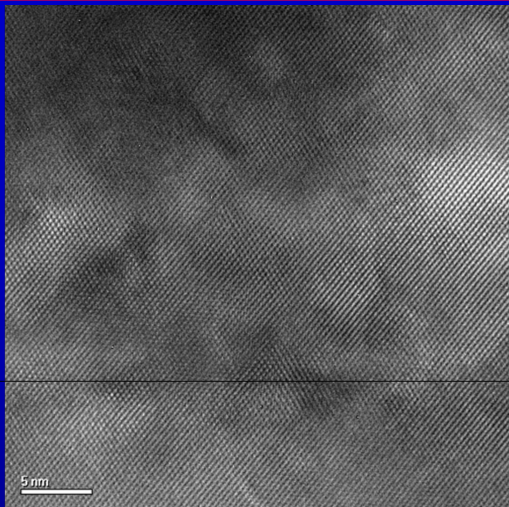




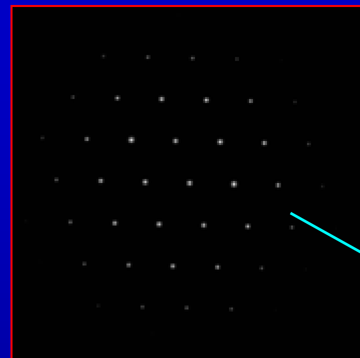
Morphology of nano particles of ZnSe at viewing angles of 0 and 60 degree tilts indicating that particles are spherical

There was very small difference in nanomorphology of ZnSe layers

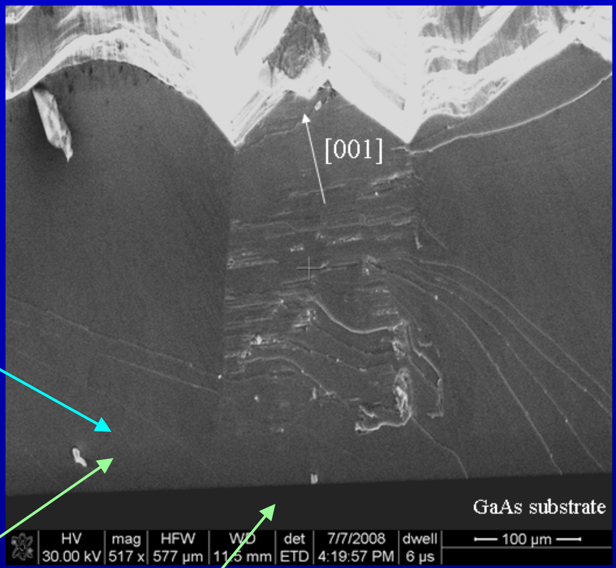
Electron Microscopy of (110) Confirms Orientation and Elemental Composition



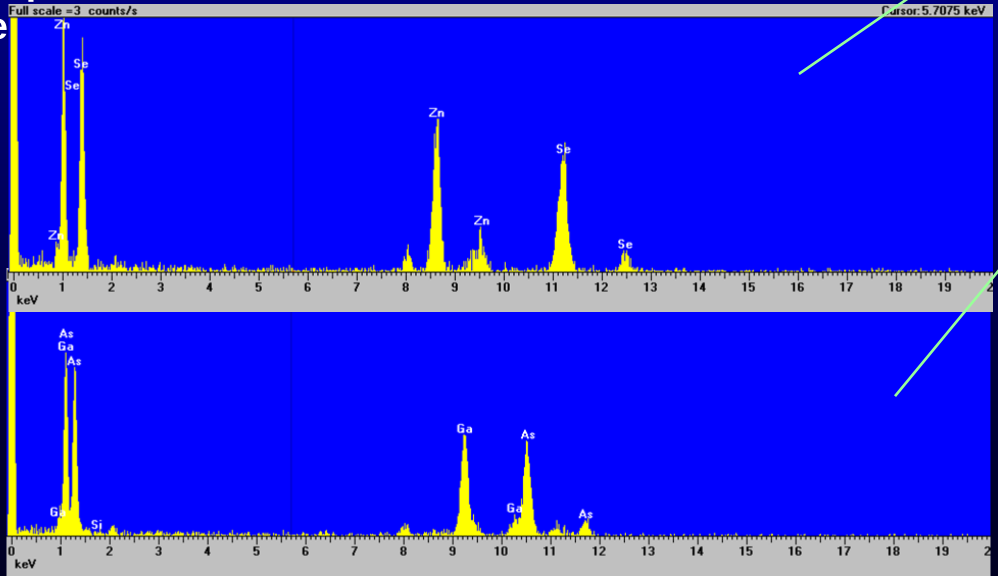
High-resolution TEM shows epitaxial alignment of ZnSe film with GaAs template; line marks the interface



Selective area diffraction shows the expected (110) projection of electron beam

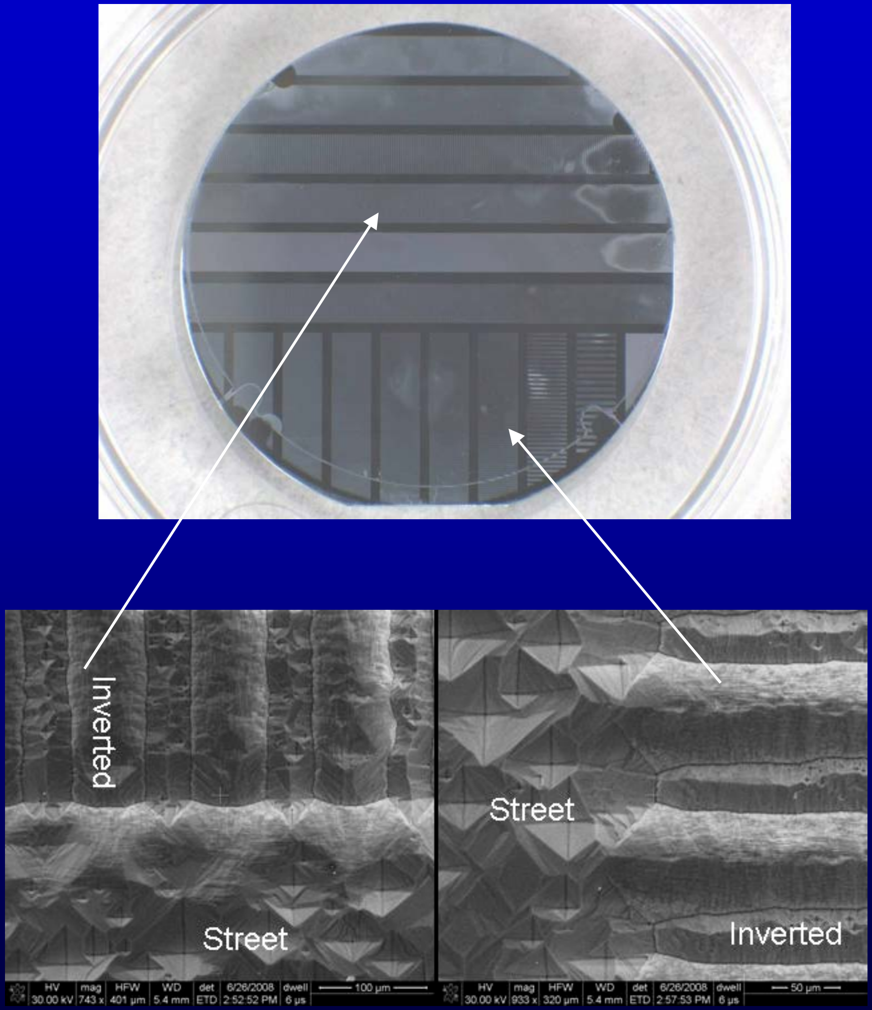


Cleaved (110) edge of grating reveals domain interfaces in SEM



Energy dispersive X-ray analysis shows the Zn and Se, and Ga and As peaks above and below the substrate-film interface, respectively.

SEM of (001) Shows Orientation Reversal in Morphology



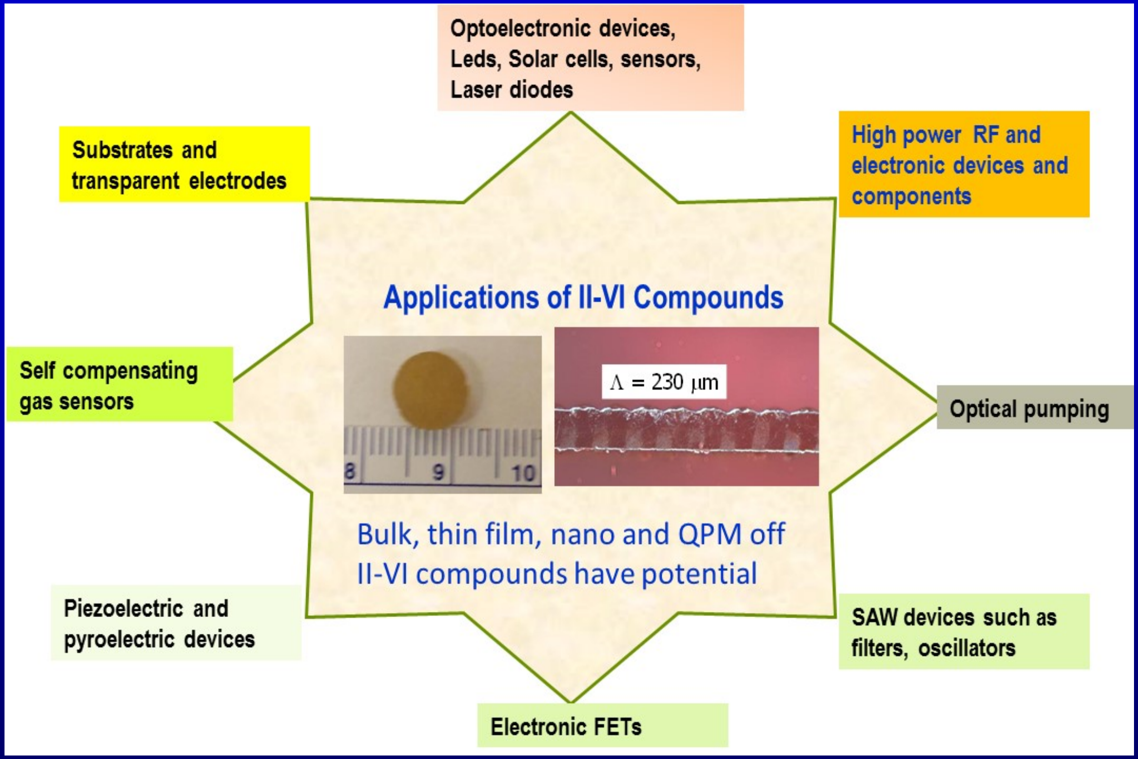
- **Morphology of individual domains switches as expected for gratings oriented perpendicular to each other**

Summary

- There is a strong need of material for MWIR and LWIR applications
- GaSe is an excellent materials, but suffers from cleavage plane.
- TAS is well developed, good for SHG applications. It has large walkoff angle.
- AgGaGeSe has great promise since it has better properties such as absorbance, transparency and no annealing or cracking compared to that of $AgGaSe_2$ and $ZnGeP_2$ crystals
- GaSe and ZnSe are excellent materials for THz sensor

ZnSe is a multifunctional material

- ZnSe is a unique material
- Flight experiment is scheduled for PVT growth
- We have grown $ZnSe_xS_{1-x}$ crystals to tailor the properties
- We have studied its transmission, emission and absorption characteristics
- We are continuing because of wide range of applications



With increasing concentration of S, quality of $ZnSe_xS_{1-x}$ decreased